228. Dediazoniations of Arene Diazonium Ions in Homogeneous Solution. Part VI[1]: Solvolyses in 2,2,2-Trifluoroethanol/Water Mixtures and Exclusion of a Potential Aryne Mechanism[2]

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Summary. The rates and products of dediazoniation of benzenediazonium tetrafluoroborate in 2,2,2-trifluoroethanol (TFE)/water mixtures has been determined. The results are *not* consistent with a mechanism in which TFE and water enter the rate-determining part of the reaction as *nucleophiles*. The influence of the solvent composition on product ratios and rates is explained as a solvent effect, the formation of a (solvated) aryl cation being the rate-determining part of the reaction. The magnitude of the preexponential factor of the *Arrhenius* equation is consistent with this interpretation. Since the solvolysis of *p*-chlorobenzenediazonium tetrafluoroborate in TFE yields no detectable *m*-products, an aryne-like mechanism is excluded.

1. Introduction. – Nucleophilic dediazoniations of arene diazonium ions are generally considered the only cases of S_N1 mechanisms in nucleophilic aromatic substitution and, therefore, the source of aryl cations [2]. Yet for several anions, linear dependence of the rates of decomposition in water on the concentration of the anion has been found by *Lewis et al.* [3]. We demonstrated recently a straightforward first-order kinetic participation of toluene, benzene, trifluoromethylbenzene, and anisole in arylations with benzenediazonium tetrafluoroborate in 2,2,2-trifluoroethanol (TFE) [4]. On the other hand, we have found [1] that benzenediazonium ions labelled with ^{15}N in the β-position, exchange nitrogen in TFE solutions under 300 atm of $^{14}N_2$. This result is consistent with the occurrence of the reverse reaction of a nitrogen molecule with a phenyl cation forming a diazonium ion.

Since arene diazonium salts are easily soluble in TFE and in water, and as these two solvents are miscible in all proportions, we investigated the products and rates of dediazoniations in the binary solvent system TFE/water over the range from 100% TFE to 100% water. It was anticipated that such experiments would determine whether or not molecules of these solvents are involved in the rate-determining step(s) of these reactions.

In addition, the results of such an investigation might be compared with other solvolyses in TFE/water mixtures which were published in recent years and which demonstrated that mixed solvent systems containing TFE with water, ethanol etc. show some unexpected peculiarities [5–7].

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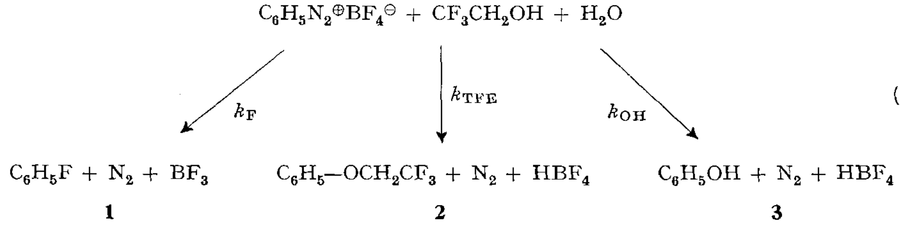
2. Dediazoniation Products of Benzenediazonium Tetrafluoroborate. – Thermal decomposition of benzenediazonium tetrafluoroborate in mixtures of water and TFE yields fluorobenzene (**1**), phenyl-2,2,2-trifluoroethyl ether (**2**) and phenol (**3**) in quantitative yield. We detected no other products.



(1)

Reactions were performed under nitrogen in the dark at 30.0 ± 0.05°. Products were analyzed by gas-liquid chromatography (GLC.). The product analyses are summarized in Fig. 1. The most striking feature of the data is the linear increase of the percentage of phenol (**3**) and respective decrease of fluorobenzene (**1**) and the phenyl ether (**2**) up to about 70% H_2O content in the solvent mixture. The phenyl ether/fluorobenzene ratio **2**:**1** is constant (= 1.82 ± 0.06) up to 40% H_2O.

It is important to note that, at lower TFE contents than about 12%, no phenylether and fluorobenzene, but only phenol is formed. This observation indicates, as discussed in the next section of this paper, that the product-determining step occurs *after* the rate-limiting step.

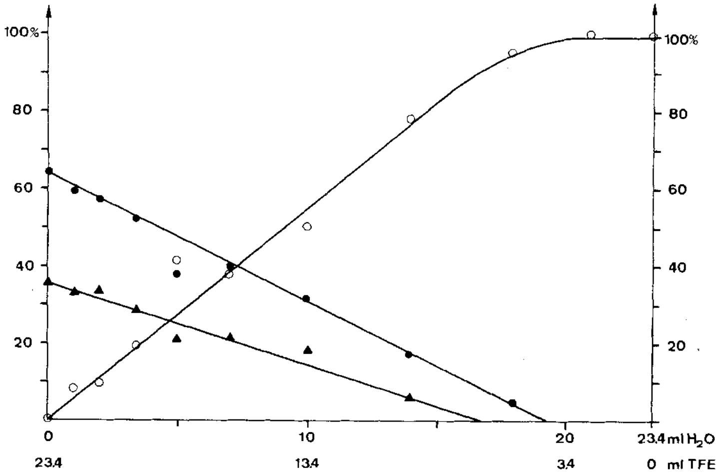


Fig. 1. *Dediazoniation products of benzenediazonium tetrafluoroborate in TFE/water mixtures*
▲ Fluorobenzene (**1**); ○ Phenyl-2′,2′,2′-trifluoroethyl ether (**2**); ● Phenol (**3**)

3. Kinetics of Dediazoniations. – The decrease in diazonium ion concentration was followed by allowing aliquot samples of the reaction mixture to react with 2-naphthol-3,6-disulfonic acid. The concentration of the resulting dye was measured spectrophotometrically [4]. In Fig. 2 the measured first-order rate constants at

30.0 ± 0.05° are plotted as a function of the solvent composition. The rate increases on addition of small amounts of water, goes through a maximum at a water content of about 20% H_2O, and then the rate decreases linearily to 100% H_2O.

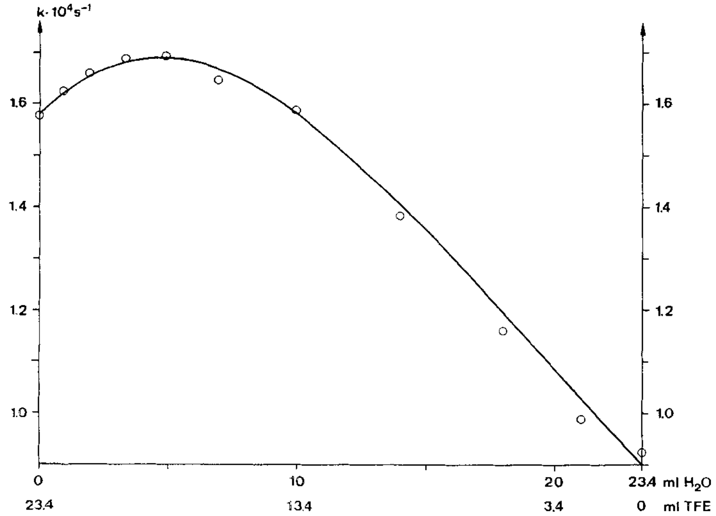


Fig. 2. *Dediazoniation rates of benzenediazonium tetrafluoroborate in TFE/water mixtures*

First of all, it is interesting to note that the rate in pure TFE is higher than in water, although water is known to be a much better nucleophile than TFE. TFE is sufficiently polar to support ionic reactions, but at the same time it is relatively non-nucleophilic. This becomes particularly evident from the analysis of *Bentley et al.* [5] who evaluated solvents with the nucleophilicity parameter N_{BS}. N_{BS} for water is −0.26 (80% $EtOH/H_2O$ being the standard) while 97% TFE has an N_{BS} value of only −2.59. N_{BS} values for these and other TFE/water mixtures have also been determined by *Raber et al.* [6].

The situation is even more strange if one assumes, in analogy to the dediazoniation with halide ions [3] and with aromatic substrates [4] mentioned in the Introduction of this paper, that water and TFE molecules, respectively, are involved in the rate-determining steps of these solvolyses. The calculated second-order rate constants would be $k_2 = 1.67 \times 10^{-6}\ \mathrm{l\,M^{-1}s^{-1}}$ for the hydroxy-dediazoniation and $k_2 = 11.3 \times 10^{-6}\ \mathrm{l\,M^{-1}s^{-1}}$ for the trifluoroethoxy-dediazoniation. Such a result is highly improbable for a reaction in which water and TFE act as nucleophilic reagents in bimolecular substitution!

In Table 1 we calculated the first-order (or pseudo-first-order) rate constants for the fluoro-, the trifluoroethoxy- and the hydroxy-dediazoniation from the measured total rate of dediazoniation and the product ratios (assuming that these three reactions are parallel competitive reactions).

These rate constants demonstrate also that there is a complex correlation between rate, nature and concentration of the solvent.

We conclude from the results summarized in Table 1, and in Fig. 1 and 2 that:

a) differences in solvation between trifluoroethanol and water affect the rate-determining part of the two solvolyses. The solvent molecules are not involved as nucleophilic reagents. The nucleophilic attack (product determining step) occurs *after* the formation of the aryl cation (rate-

Table 1. *Rate constants for competitive dediazoniations of benzenediazonium tetrafluoroborate in TFE/water mixtures at 30.0 ± 0.05°*

TFE		Rate constants (s^{-1})			
vol %	mole fraction	fluoro-dediazoniation $k_F \cdot 10^4$	trifluoroethoxy-dediazoniation $k_{TFE} \cdot 10^4$	hydroxy-dediazoniation $k_{OH} \cdot 10^4$	total $k \cdot 10^4$
100	1.00	0.562	1.009	0	1.571
95.7	0.85	0.535	0.963	0.128	1.626
91.4	0.73	0.550	0.952	0.160	1.662
85.5	0.59	0.478	0.878	0.333	1.689
78.6	0.47	0.350	0.634	0.706	1.690
70.1	0.35	0.359	0.653	0.636	1.648
57.3	0.25	0.269	0.516	0.802	1.587
40.2	0.14	0.075	0.226	1.080	1.381
23.1	0.069	0	0.057	1.104	1.161
10.3	0.027	0	0	0.988	0.988
0	0	0	0	0.927	0.927

limiting step). Conductance studies in TFE reported by *Evans et al.* [8] lead to the conclusion that this solvent enhances the solvation of anions and diminishes the solvation of cations. This result is consistent with our interpretation, and

b) the fluorodediazoniation reaction is not a reaction between free diazonium ions and tetrafluoroborate ions, but a reaction within an ion pair containing these two ions. This conclusion is substantiated by the fact that fluorobenzene as a product cannot be found in water (where ion pairs are unlikely to be formed), but is found in increasing percentages in solutions containing higher fractions of TFE, *i.e.* in a solvent which favours ion pairs. This conclusion is also consistent with the fact that the classical *Schiemann* reaction is not carried out in (aqueous) solution but rather by heating solid arene diazonium tetrafluoroborate [9]. It also agrees with the result of *Swain et al.* [10] that it is the tetrafluoroborate anion and not a fluoride ion which acts as a nucleophile in the *Schiemann* reaction carried out in methylene chloride solution.

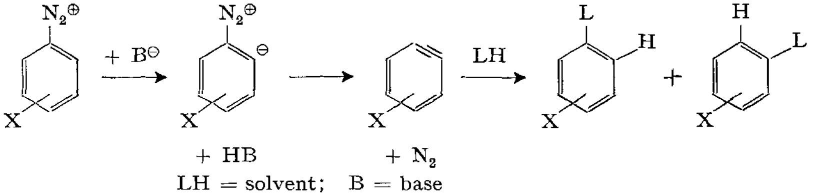
In addition we determined the temperature dependence of the solvolysis of benzenediazonium tetrafluoroborate in TFE between 14.9° and 50.1° (Data in the Experimental Part). The analysis of the rate data with the *Arrhenius* equation gave an activation energy $E_a = 116.7$ kJ/mol (28.27 kcal/mol) and a preexponential factor $A = 3.77 \times 10^{16}\ s^{-1}$. The A-factor is consistent with a first-order rate-determining step, but hardly with a rate-limiting attack of the nucleophile (solvent) on the arene diazonium ion [11].

We also measured the *Arrhenius* parameter for the dediazoniation in the presence of benzene. Under these conditions biphenyl is formed in a heterolytic reaction [4] in addition to the usual reaction products **1** and **2**. The fact that these parameters ($E_a = 114.2$ kJ/mol $= 27.65$ kcal/mol; $A = 1.46 \times 10^{16}\ s^{-1}$) are very similar to those of the pure solvolysis indicate that in aryl-dediazoniation and in solvolytic dediazoniation the same intermediate, namely a solvated aryl cation is involved.

As discussed in a previous paper [1] we suspect that the aryl cation is formed in two (or more) steps. This part of the reaction is still under investigation.

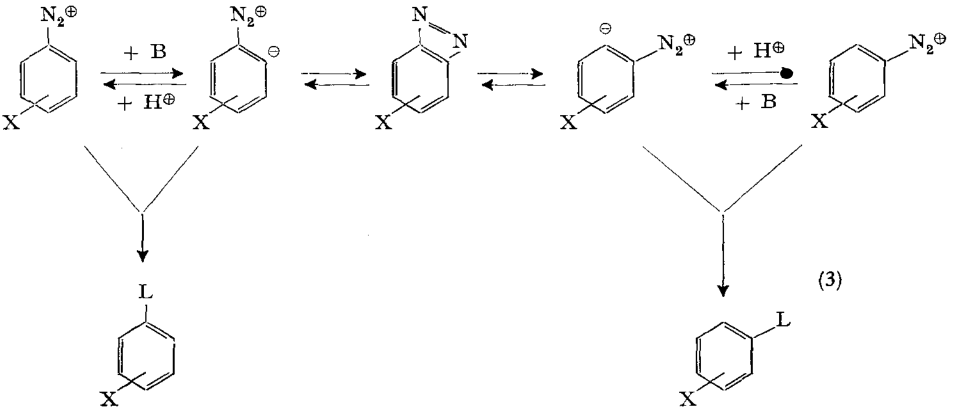
Independently, *Swain et al.* [10] came to conclusions which are consistent with our explanations given in this and the preceding paper of this series [1].

4. Exclusion of an Aryne Mechanism. – It has been shown by *Cadogan et al.* [12] that under certain conditions and with suitably substituted arene diazonium salts a dediazoniation mechanism involving an aryne intermediate takes place (2).



(2)

We checked this possibility for our TFE system because such a mechanism *might* explain the N_α–N_β rearrangement of the two nitrogen atoms of an arene diazonium ion. *Lewis et al.* [13] found small extents of isotopic scrambling (1–2%) in aqueous solution. We have recently demonstrated that this scrambling takes place at a significantly higher relative rate in TFE [1] [14]. The N_α–N_β rearrangement could be visualized by mechanism (3) which is related to the first step of (2).



(3)

Obviously mechanism (3) gives isomeric solvolysis products, depending on the type and position of the substituent X.

Therefore we carefully investigated the dediazoniation products of *p*-chlorobenzenediazonium tetrafluoroborate (X = *p*-Cl) in TFE as solvent (L = $-OCH_2CF_3$ and –F). GLC.-analysis of the products was carried out under condition which allowed simultaneous detection of *m*- and *p*-fluorochlorobenzene as well as *m*- and *p*-chlorophenyl-2′,2′,2′-trifluoroethyl ether. No *m*-derivatives could be found within the limits of detection (0.5% to 1%). Products found are given in Table 2.

Table 2. *Products of solvolysis of* p-*chlorobenzenediazonium tetrafluoroborate in TFE at 74°*

p-$ClC_6H_4N_2^\oplus BF_4^\ominus$	TFE	*p*-ClC_6H_4F	*p*-$ClC_6H_4OCH_2CF_3$
0.0051 mol	40 ml	31.4%	68.6% [a]
0.0034 mol	30 ml	35.6%	64.4% [a]

[a] No other products.

Therefore, the reaction does not proceed *via* mechanism (3) to a measurable extent.

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5. Experimental Part. 5.1. *Product Determination.* Solutions of 0.1068 mol/l benzenediazonium tetrafluoroborate in 23.4 ml TFE, water or TFE/water mixtures were solvolysed under a nitrogen atmosphere in the dark at 30.0 ± 0.05°. For details of the experimental procedure see [4]. Results are given in Table 3. The sum of the yields was between 91 and 104% relative to the amount of the diazonium salt. In Table 3 these yields are normalized to 100%.

Table 3. *Products of dediazoniation of 0.1068* M *benzenediazonium tetrafluoroborate in TFE/water mixtures* (30.0 ± 0.05°)

TFE		H_2O		C_6H_5F (**1**, %)	$C_6H_5OCH_2CF_3$ (**2**, %)	C_6H_5OH (**3**, %)
ml	mol fraction	ml	M			
23.4	1.00	0	0	35.8	64.2	0
22.4	0.85	1.0	2.39	32.9	59.2	7.9
21.4	0.73	2.0	4.74	33.1	57.3	9.6
20.0	0.59	3.4	8.08	28.3	52.0	19.7
18.4	0.47	5.0	11.88	20.7	37.5	41.8
16.4	0.35	7.0	16.62	21.8	39.6	38.6
13.4	0.25	10.0	23.76	17.0	32.5	50.5
9.4	0.14	14.0	33.25	5.4	16.4	78.2
5.4	0.069	18.0	42.74	0	4.9	95.1
2.4	0.027	21.0	49.87	0	0	100
0	0	23.4	55.55	0	0	100

5.2. *Kinetic Measurements.* The spectrophotometric method used was already described [4]. Results at 30.0° in TFE/water mixtures are given in Table 1; those for the determination of the rate dependence on the temperature with and without addition of benzene are collected in Table 4.

Table 4. *Rate of dediazoniation in TFE with and without addition of benzene*

$C_6H_5N_2^{\oplus}\ BF_4^{\ominus}$ mol/l	C_6H_6 ml[a])		Products (%)			Rate s^{-1}
			C_6H_5F	$C_6H_5OCH_2CH_3$	$C_6H_5C_6H_5$	
0.1068	–	14.9°	32.6	67.4	–	$1.401 \cdot 10^{-5}$
0.1068	–	30.0°	36.0	64.0	–	$1.574 \cdot 10^{-4}$
0.1068	–	30.0°	39.1	60.9	–	$1.604 \cdot 10^{-4}$
0.1068	–	30.0°	35.5	64.5	–	$1.582 \cdot 10^{-4}$
0.1068	–	30.0°	34.9	65.1	–	$1.571 \cdot 10^{-4}$
0.1068	–	49.8°	32.0	68.0	–	$2.797 \cdot 10^{-3}$
0.1068	–	50.1°	34.1	67.4	–	$3.057 \cdot 10^{-3}$
0.1041	3.33	14.9°	c)	52.2	27.7	$1.571 \cdot 10^{-5}$
0.1041	3.33	30.0°	c)	53.9	25.8	$1.701 \cdot 10^{-4}$
0.1041	3.33	30.0°	c)	45.0	22.1	$1.700 \cdot 10^{-4}$
0.1041	3.33	49.8°	c)	56.4	23.2	$2.848 \cdot 10^{-3}$
0.1041	3.33	49.9°	c)	51.5	25.2	$2.949 \cdot 10^{-3}$

a) Total volume in all runs 23.4 ml.
b) ± 0.05°.
c) Not determined.

5.3. *Dediazoniation of* p-*Chlorobenzenediazonium Tetrafluoroborate. m*-Chlorophenyl-2′,2′,2′-trifluoroethyl ether was synthesized from *m*-chlorobenzenediazonium tetrafluoroborate in an analogous way as described [4] for the *p*-isomer. The purity of all reference compounds was checked by GLC.

Dediazoniation of *p*-chlorobenzenediazonium tetrafluoroborate was made under nitrogen in the dark at the boiling temperature of TFE (74°); see also Table 2. Analysis of the mixture of products was made in the usual way [4]. For the separation of the products the columns described in Table 5 were used.

Table 5. *Columns for product separations*

Separation	*m*/*p*-fluorochlorobenzene		*m*/*p*-chlorphenyl-trifluoroethyl ether	
Column	1	2	3	4
Filling	10% Apiezon L on Chromosorb W 80/100	20% Carbowax 1500 on Chromosorb W AW 60/80	as column 1	as column 2
Length	5 m	4.8 m	5 m	4.8 m
Temperature	80°	100°	120°	145°
Standard	Toluene	Toluene	Dimethylresorcinol	Dimethylresorcinol
Helium (ml/min)	30	40	30	40–50
Result	Separation not complete, but sufficient to detect 1% *m*-isomer	Separation complete, slightly disturbed by TFE	Separation not complete, but sufficient to detect 1% *m*-isomer	Good separation

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